

## PATENT SPECIFICATION

490,930



Convention Dates (Germany) :

Dec. 20, 1935 No. 35074/36

June 22, 1936 No. 35075/36

Aug. 17, 1936 No. 35076/36

Corresponding Applications  
in United Kingdom  
dated Dec. 21, 1936(One Complete Specification Left under Section 91 (2) of the Patents and Designs  
Acts, 1907 to 1932)

Specification Accepted : Aug. 22, 1938.

## COMPLETE SPECIFICATION

## ERRATA

5

SPECIFICATION No. 490,930.

Page 1, line 48, for " reaction " read  
" reactions "

10

Page 1, line 53, for " might " read  
" must "

Page 1, line 94, for " is " read " it "

THE PATENT OFFICE,

October 13th, 1938.

15

which have been produced by cracking liquid hydrocarbons that boil above 100° C. and which have been obtained by the catalytic conversion at normal pressure and at moderately raised temperatures from mixtures of carbon monoxide and hydrogen.

In cracking the hydrocarbons mentioned, the conditions are so selected that a benzine which has a high content of unsaturated hydrocarbons but contains little or no aromatic hydrocarbons, is produced, which is then wholly or partly—that is to say after the distilling off of particular fractions—treated in known manner with anhydrous aluminium chloride or other condensation agents, viscous oils being produced by condensation and polymerization. The condensation agent initially employed in the condensation of the mixtures of hydrocarbons containing olefines can be used repeatedly for one particular condensation reaction, if during the succeeding condensation reactions the conversion temperature is suitably raised. This much repeated use of the same catalyst for fresh condensation reaction reduces the consumption of condensation agents very considerably. However, after many repeated conversions with the same catalyst, the effectiveness of the catalyst, is finally so reduced that it might be

[Price 1/-]

(either continuously or intermittently) raising the conversion temperature during the course of the condensation reaction. This method has the great advantage that with a given quantity of aluminium chloride, substantially larger quantities of benzine can be converted in one charge than is possible if unsaturated benzines with the same quantity of aluminium chloride are converted with the condensation temperature unaltered. In order in this way to convert a large quantity of unsaturated benzines, with a given quantity of aluminium chloride, it was necessary hitherto to divide the benzine into a number of charges and again to use the condensation agent employed in the preceding condensation reaction while raising the conversion temperature, during the conversion of the next benzine charge. In this way it has hitherto been necessary to employ a much greater proportion of catalyst and to work up the reaction products repeatedly while in the method according to the invention when working up a like quantity of benzine these operations have to be carried out once only.

It has further been found that it is possible to economise in condensation agents such as aluminium chloride by adding, after reaching the highest temperature—that is to say after the

## PATENT SPECIFICATION

490,930



## Convention Dates (Germany) :

Dec. 20, 1935 No. 35074/36

June 22, 1936 No. 35075/36

Aug. 17, 1936 No. 35076/36

Corresponding Applications  
in United Kingdom  
dated Dec. 21, 1936(One Complete Specification Left under Section 91 (2) of the Patents and Designs  
Acts, 1907 to 1932)

Specification Accepted : Aug. 22, 1938.

## COMPLETE SPECIFICATION

## Process for producing Lubricating Oils

We, RUHRCHEMIE AKTIENGESellschaft, of Oberhausen-Holtten, Germany, a body corporate organised and existing under the Laws of the German State, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

- 10 It is known in connection with the production of synthetic lubricating oils to start with mixtures of liquid hydrocarbons containing unsaturated hydrocarbons, and to condense the mixtures by using suitable condensation agents.
- 15 Suitable substances may be obtained, for example, by cracking or by the catalytic dehydrogenation of hydrocarbon oils. It has been found preferable to make use of benzines which are rich in olefines and which have been produced by cracking liquid hydrocarbons that boil above 100° C. and which have been obtained by the catalytic conversion at normal pressure
- 20 and at moderately raised temperatures from mixtures of carbon monoxide and hydrogen.

- In cracking the hydrocarbons mentioned, the conditions are so selected that
- 30 a benzine which has a high content of unsaturated hydrocarbons but contains little or no aromatic hydrocarbons, is produced, which is then wholly or partly—that is to say after the distilling off of particular fractions—treated in known manner with anhydrous aluminium chloride or other condensation agents, viscous oils being produced by condensation and polymerization. The condensation agent initially employed in the condensation of the mixtures of hydrocarbons containing olefines can be used repeatedly for one particular condensation reaction, if during the succeeding
- 45 condensation reactions the conversion temperature is suitably raised. This much repeated use of the same catalyst for fresh condensation reaction reduces the consumption of condensation agents very considerably. However, after many
- 50 repeated conversions with the same catalyst, the effectiveness of the catalyst, is finally so reduced that it might be

replaced by fresh catalyst, as any further raising of the condensation temperature would adversely affect the reaction.

According to the invention it is possible to economise in condensation agents in still greater measure by employing, when carrying out the first condensation reaction, only a small quantity of aluminium chloride or other condensation agent in relation to the benzine which is rich in olefines, the quantity being so small that it would be by no means sufficient to obtain during a single temperature stage a sufficient conversion of the benzine in the carrying out of the condensation reaction. Complete conversion of the benzine which is rich in olefines while carrying out condensation in a single stage, is obtained according to the invention by gradually (either continuously or intermittently) raising the conversion temperature during the course of the condensation reaction. This method has the great advantage that with a given quantity of aluminium chloride, substantially larger quantities of benzine can be converted in one charge than is possible if unsaturated benzines with the same quantity of aluminium chloride are converted with the condensation temperature unaltered. In order in this way to convert a large quantity of unsaturated benzines, with a given quantity of aluminium chloride, it was necessary hitherto to divide the benzine into a number of charges and again to use the condensation agent employed in the preceding condensation reaction while raising the conversion temperature, during the conversion of the next benzine charge. In this way it has hitherto been necessary to employ a much greater proportion of catalyst and to work up the reaction products repeatedly while in the method according to the invention when working up a like quantity of benzine these operations have to be carried out once only.

It has further been found that it is possible to economise in condensation agents such as aluminium chloride by adding, after reaching the highest temperature—that is to say after the

[Price 1/-]

completion of the conversion—a small quantity of fresh aluminium chloride to the spent aluminium chloride, whereupon the conversion of, for example, a new charge of cracked benzine can commence again at a low temperature. No broad claim is made to this feature in view of the claims which we have made in our Specification No. 473,935.

The following example explains the process more exactly:

EXAMPLE I.

1000 gm. of a cracked benzine of specific gravity 0.692 at 20° C. containing 45% of unsaturated hydrocarbons were charged with 10 gm. of anhydrous aluminium chloride and subjected to a condensation reaction while the temperature was being gradually and continuously raised. The temperature of originally 20° C. was raised continuously to 100° C. during the course of 120 hours. After the conversion had ceased, the layer of benzine containing the lubricating oil formed was separated from the contact layer that consists of aluminium chloride and double compounds of aluminium chloride, and from it 424 gm. of lubricating oil were extracted by distillation. The proportion of lubricating oil secured to the aluminium chloride introduced thus amounted to 42:1. After the addition of a small quantity of fresh anhydrous aluminium chloride (about 10 to 20% of the quantity first added) to the layer of catalyst separated off, the latter can be used again for the conversion of cracked benzine commencing again at low temperatures such as 20° C.

It has furthermore been found necessary to absorb at suitable temperatures the heat generated during the condensation reaction in every stage of condensation. The heat must not therefore be deliberately absorbed as has hitherto been the practice, but care must be taken that from the commencement of the reaction the heat generated is absorbed only to such an extent that a slow rise in temperature to a predetermined final temperature results within the condensation period. The following experiments are put forward to explain the conditions:

A cracked benzine containing aluminium chloride was poured into a well insulated vessel and stirred. The heat of polymerization heated the mixture rapidly to 70° C. At this temperature cooling was started and the heat generated absorbed. During the experiment it was found that strong polymerization took place but that condensation products of preponderatingly low molecular weight were obtained. Where the same cracked

benzine was caused to react in the same vessel and with the same quantity of aluminium chloride, but care was taken that the heat generated was absorbed from the outset to such an extent that a slow rise of temperature to 70° C. took place within a period of 12 hours, a very large yield of valuable highly polymer oils was obtained as the polymerization product.

Where on the other hand, the cooling action was carried out in a third experiment to too great an extent, there was no rise of temperature, the reaction was arrested and practically no polymerization took place.

It was further found advisable to begin the condensation of the unsaturated hydrocarbons at as low temperatures as possible, for example, between 0 and 30° C., and to reduce the too rapid reaction by suitable cooling in such manner that only a slow rise of temperature took place in the conversion vessel due to the heat generated in polymerization and that the final temperature set up as the result of the condensation period of 6 to 20 hours did not exceed 50 to 80° C. in the case of producing heavy oils and 100 to 120° C. in the case of producing light oils.

The benzine charge which is undergoing reaction can be cooled either by external cooling or by direct or indirect internal cooling or by a combination of both, it being advantageous to assist the distribution of the heat in the reaction vessel by vigorously stirring the reaction mixture.

Exact control of temperature in these reactions is rendered difficult by the physical properties of the contact layers produced with the condensation agent, for example  $AlCl_3$ , during the conversion of the unsaturated oils. On the one hand external cooling combined with the stirring of the conversion mixture is usually insufficient for absorbing the large quantities of heat generated during the condensation reaction, sufficiently rapidly from the conversion vessel, and on the other hand by reason of the properties of the contact layers it is in practice not possible to absorb additional heat by employing suitable cooling surfaces. It has previously been proposed to produce viscous oils by condensation of mixtures of unsaturated hydrocarbons by adding neutral oils to the reaction mass in order thus to reduce the quantity of heat generated and the concentration of the reacting substances. This method has however the disadvantage that large quantities of diluents must be added and after the reaction is complete, removed by distillation from the viscous oils produced.

It has also been found to be an advantage to add to the unsaturated oils to be converted, neutral low-boiling substances such as propane, butane or pentane or mixtures of these hydrocarbons by the evaporation of which the heat is drawn off from the reaction mass. Measurements have shown that the quantities of heat per kg. of oil generated during the condensation of the lubricating oil amount to 150 to 200 Kcal. In order to absorb quantities of heat at particular temperatures the maintenance of which is important to polymerization, it is possible to proceed in various ways.

For example, one may add, at normal pressure, to the reaction mass which is being rapidly stirred, such a quantity of light-boiling hydrocarbons that the heat absorbed by the evaporation of the quantity introduced corresponds to the generated heat of condensation and polymerization, the substances issuing in gaseous form being reliquefied outside the reaction vessel.

However, a certain quantity of light-boiling substances may be added at the commencement to the conversion vessels which are provided with counter-current coolers, these light-boiling substances evaporating during the reaction but being condensed in the counter-current coolers. The maintenance of a particular reaction temperature is effected in this method by simultaneously adjusting the condensation temperature and the corresponding vapour pressure by the cooling agent which evaporates while in circulation, recondenses and returns to the stirred vessel.

In order with this method to avoid the pressures rising in the conversion vessels beyond the desired limits when the reaction temperatures become necessarily higher, it is under certain conditions advantageous to employ at higher reaction temperatures cooling agents which boil at correspondingly higher temperatures.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for producing lubricating oils by the condensation of benzines produced by catalytic conversion of mixtures of hydrogen and carbon monoxide and containing unsaturated hydrocarbons by using suitable condensation agents, characterised in that the

condensation temperature is gradually raised, continuously or in stages, during conversion and that the condensation agent is employed in a quantity which is insufficient for complete conversion in a single temperature stage and that the catalyst separated off from the reaction product is used for the conversion of a new charge of benzine again commencing with low temperatures.

2. A process according to claim 1, characterised in that the catalyst which is reduced in effectiveness after one or more condensations have taken place is regenerated by the addition of small quantities of fresh catalyst.

3. A process according to claim 1, characterised in that the original reaction temperature is advantageously between 0 and 30° the reaction temperature being raised slowly during the reaction.

4. A process according to claim 1, 2 or 3 characterised in that the changes of temperature in the conversion vessel are controlled in such manner that the temperature is only gradually raised continuously or in stages by the heat of polymerization, it being necessary for producing highly viscous oils that a final condensation temperature of from 50 to 80° C. shall not be exceeded in the reaction mixture, and for producing less viscous oils a final condensation temperature of from 100 to 120° C. shall not be exceeded.

5. A process according to claim 1, 2, 3 or 4 characterised in that neutral substances that boil at low temperatures are added to the oils to be converted, for the purpose of regulating temperature, which substances are caused to evaporate by the heat generated during the reaction.

6. A process according to claim 1, 2, 3, 4 or 5, characterised in that the cooling agent evaporates while in circulation, recondenses and returns to the stirred vessel, the desired reaction temperature being maintained by the simultaneous adjustment of the condensation temperature and of the corresponding vapour pressure.

7. A process according to claim 1, 2, 3, 4, 5 or 6, characterised in that liquefied propane, butane, pentane or mixtures of these hydrocarbons or of their unsaturated homologues are used as the indifferent low-boiling cooling agent.

Dated the 21st day of December, 1936.  
EDWARD EVANS & CO.,  
40/43, Chancery Lane, London, W.C.2,  
Agents for the Applicants.